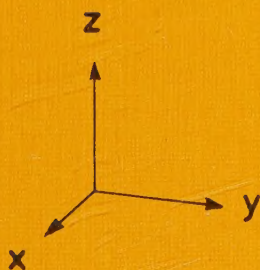


EMPTY SPACE AND STRUCTURE BUILDING PRINCIPLES

HARRY NYMAN



LUND 1979

EMPTY SPACE AND STRUCTURE BUILDING PRINCIPLES

AVHANDLING FÖR TEKNOLOGIE DOKTORSEXAMEN



Avhandlingen kommer att försvaras vid offentlig disputation å
Kemicentrum, hörsal D, fredagen den 12 oktober 1979 kl 10.15

av

Harry Nyman

Civ ing, Vrml



Empty Space and Structure Building Principles

Harry Nyman

Lund 1979

Thesis. Inorganic Chemistry 2

Chemical Center, University of Lund

P.O. Box 740, S-220 07 Lund 7

Sweden

Harry Nyman

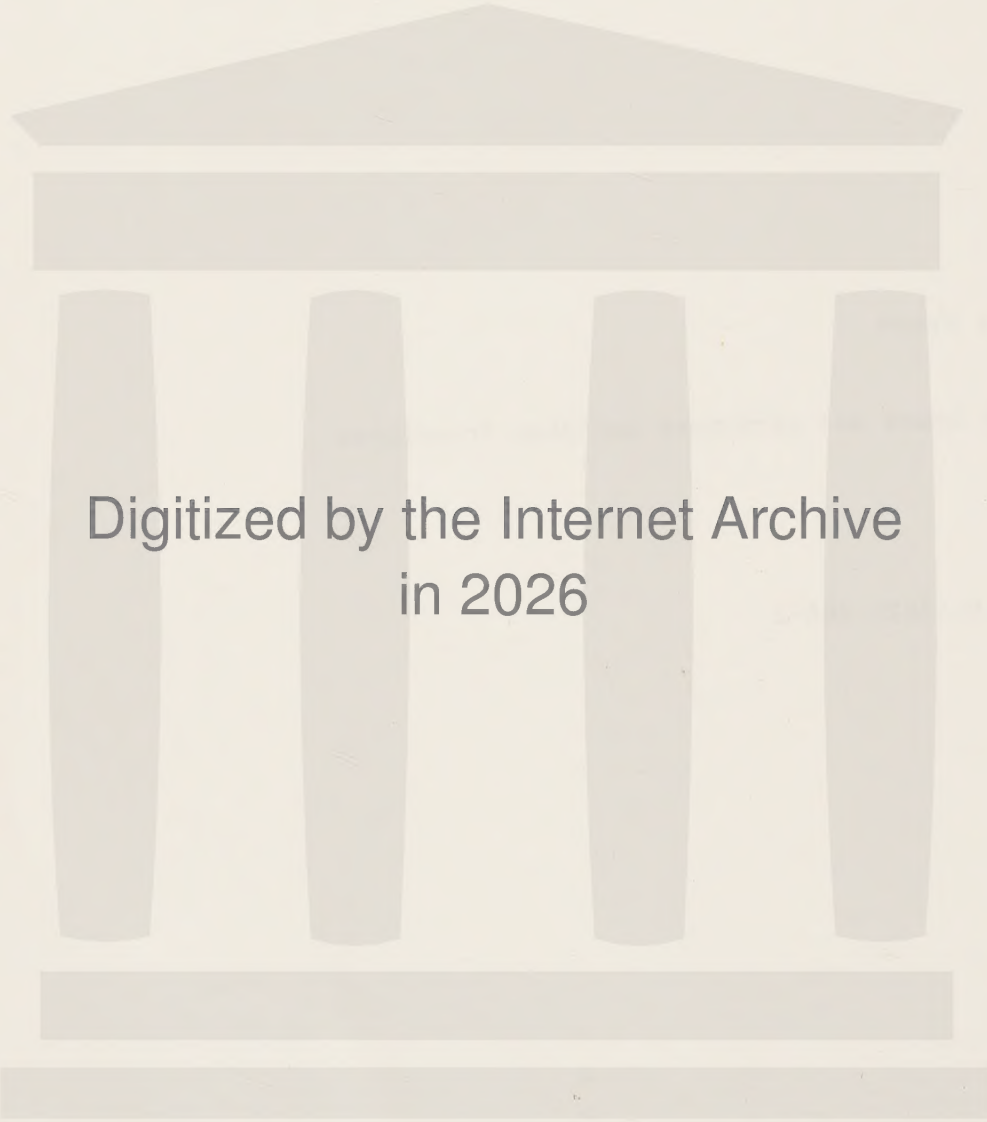
Empty Space and Structure Building Principles

ISBN 91-7222-266-2

Printed by

Reprocentralen, Lunds Universitet

Lund 1979



Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41553411_0095

CONTENTS

INTRODUCTION	page 5
1. THE RHOMBIC PRISM	7
2. THE PYROCHLORE UNIT	15
3. THE "STELLA QUADRANGULA"	24
CONCLUDING REMARKS	36
ACKNOWLEDGEMENTS	40
REFERENCES	41
APPENDIX	44

INTRODUCTION

Different kinds of coordination polyhedra are frequently used in the description of inorganic crystal structures in order to simplify the 3-dimensional picture of the structure. Sometimes it is possible to describe an array of atoms with different sets of polyhedra, e.g. a fcc structure can be described in terms of edge-sharing octahedra and/or corner-sharing tetrahedra. This means that if a structure is described with one set of centered polyhedra, the empty spaces between these can also be described with another set of polyhedra, which are non-centered or empty.

The use of empty polyhedra to describe crystal structures has two advantages; 1) the building elements are small, e.g. octahedra and tetrahedra, and 2) often therefore less distorted.

The different ways in which any given structure can be described is well illustrated by reference to cementite, Fe_3C . It can be described in terms of layers of edge and corner-sharing trigonal prisms of iron atoms, each prism centered by a carbon atom. The prisms are distorted to give a short Fe-Fe distance. On the other hand, the structure can also be described as a twinning of *hcp* (1). In this way the almost perfect, but empty octahedra of iron create in the twin-planes distorted trigonal prisms, which results in the short Fe-Fe distances mentioned above.

Not only single polyhedra, but also small groups of polyhedra, filled or empty, constituting a building block sometimes called a cluster, can be useful in the description of crystal structures.

This work summarises some attempts to describe known structures in terms of new polyhedra or clusters of polyhedra. The structure building elements dealt with here are:

1. The rhombic prism (2).
2. The pyrochlore unit (3).
3. The stella quadrangula (4, 5).

1. THE RHOMBIC PRISM

An ideal rhombic prism can be thought of as two parallel trigonal prisms with a common square face. It occurs in some structures (2) and is usually tetra-capped, with atoms outside the square faces.

In an ideal rhombic prism there are obviously two different distances from the centre to the corners; four close corners in the shape of a square and four more distant ones in the shape of a rectangle perpendicular to the square. One might therefore expect to find cations which prefer square-planar coordination in the centre of rhombic prisms, and for instance for Pd^{2+} , Cu^{2+} and Mn^{3+} this is the case.

The structures of $\alpha\text{-PdCl}_2$ and PdS contain rhombic prisms (2). In both structures the prisms are a little distorted, but in different ways. Palladium in $\alpha\text{-PdCl}_2$ is situated in an almost perfect square of chlorine atoms but the rectangle is elongated, see Fig. 1 and the prism is unsymmetrically capped with two chlorine and two palladium atoms. In PdS the central square is distorted to a rectangle and the uncapped prisms are shaped as shown in Fig. 2 and 3. The main advantage in using rhombic prisms in the description of these two structures, even though they are distorted, is that it offers the possibility of comparison with other known structures very easily.

In the description of a structure, the question of which set of polyhedra should be used often arises. In general the final choice depends mostly on the purpose of the description. Such a structure is the skutterudite-type structure, named after the mineral skutterudite, CoAs_3 . One way of describing skutterudite is to relate it to perovskite (6), another way is to use rhombic prisms.

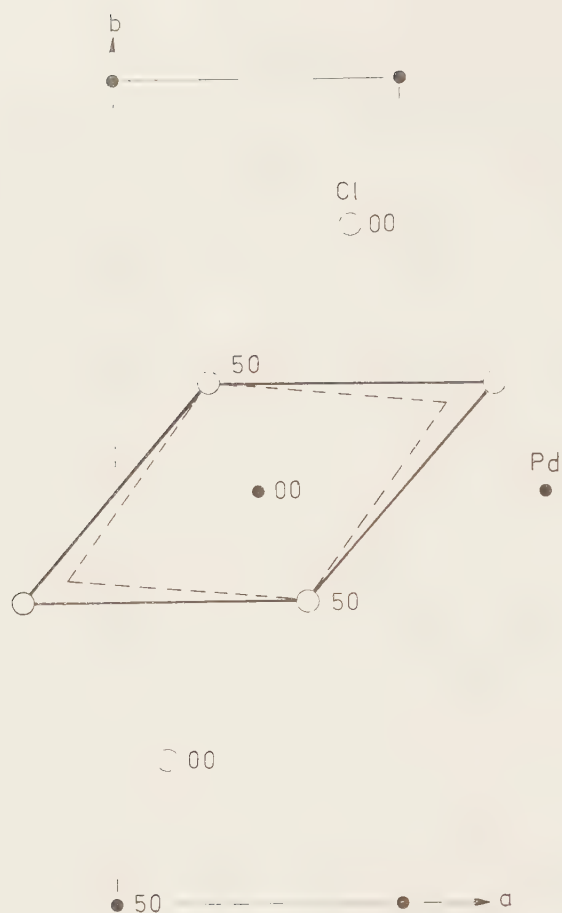


Fig. 1. The structure of α -PdCl₂ projected along 010. The hatched lines indicate an ideal rhombic prism.

If the octahedra in ideal ReO₃ are rotated about four different $\langle 111 \rangle$ directions the cuboctahedra between the ideal octahedra collapse into distorted icosahedra and distorted tetracapped rhombic prisms. On the other hand, the same structure is obtained by stacking ideal rhombic prisms in the way shown in Fig. 4, where each prism is tetracapped by corners of adjacent prisms. The interstices in the framework are octahedral and icosahedral, both slightly distorted.

If the edge of the ideal rhombic prism is d the structure can be expressed as follows:

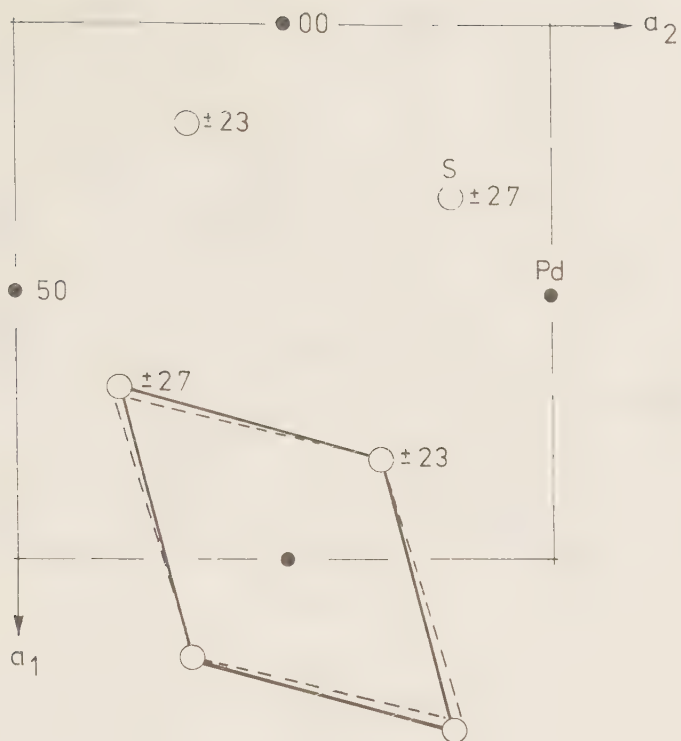


Fig. 2. Part of the structure of PdS projected along 001.
The hatched lines indicate an ideal rhombic prism.

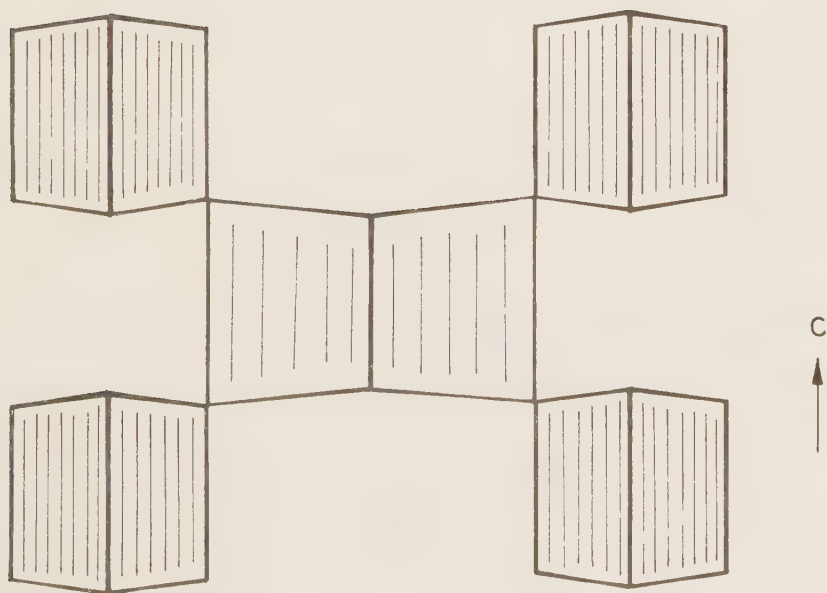


Fig. 3. The deformation of the rhombic prisms in PdS.

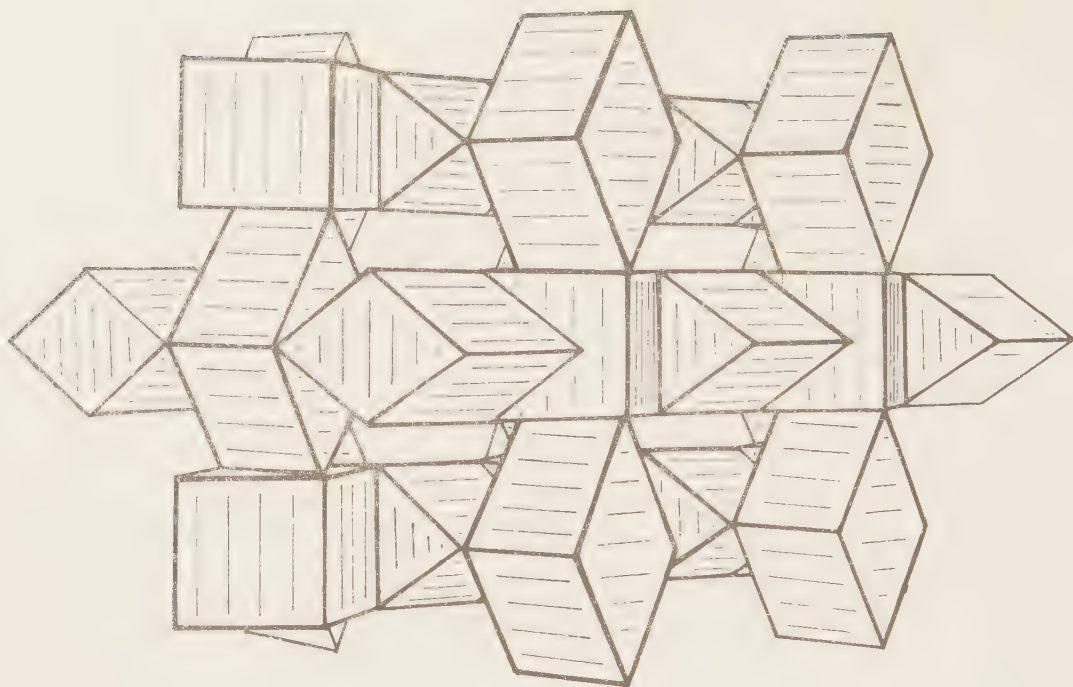


Fig. 4. The way of stacking rhombic prisms to get the skutterudite-type structure.

Space group $Im\bar{3}$ (No. 204)

Unit cell edge $a = d(1 + \sqrt{3})$

Centre of icosahedra	2(a)	000; 1/2, 1/2, 1/2
" " octahedra	8(c)	1/4, 1/4, 1/4, etc.
" " rhombic prisms	6(b)	0, 1/2, 1/2, etc.
Corners	24(g)	0, y, z, etc.

where

$$y = \frac{d}{2d(1 + \sqrt{3})} = 0.183$$

and

$$z = \frac{d\sqrt{3}}{2d(1 + \sqrt{3})} = 0.317$$

Since the only variable parameters in the structure are y and z it is easy to compare the model with some known members of this family of structures.

Table I. The variable parameters of compounds with the skutterudite-type structure.

	y	z	References
Ideal rhombic prisms	0.183	0.317	(2)
Ideal octahedra*	0.186	0.301	(2, 6)
CoAs ₃	0.15	0.35	(7)
CoP ₃	0.1453	0.3482	(8)
Sc(OH) ₃	0.182	0.307	(9)
WAl ₁₂	0.184	0.309	(10)
NaMn ₇ O ₁₂	0.1828	0.3132	(11)
CaCu ₃ Mn ₄ O ₁₂	0.182	0.303	(12)
ThCu ₃ Mn ₄ O ₁₂	0.177	0.299	(13)
LaFe ₄ P ₁₂	0.1504	0.3539	(14)

* The parameters given for ideal octahedra + ideal icosahedra in an earlier paper (2) are wrong.

It should be noted that in none of the above structures are the rhombic prisms ideal, but in some cases there is not much distortion.

To get a square around the 6(b) position, in the centre of the rhombic prism, the y and z parameters must satisfy the "Oftedal relation", $y + z = 1/2$ (15). A beautiful example of this is NaMn₇O₁₂ (11), in which y and z values are close to the ideal rhombic prism and almost satisfy the relation $y + z = 1/2$, see Table I. NaMn₇O₁₂ has three different O-O distances in the rhombic prisms, $2.729(2) \times 2 \text{ \AA}$, $2.689(2) \times 8 \text{ \AA}$ and $2.670(2) \times 4 \text{ \AA}$ with a mean value = 2.689 Å.

All the remaining O-O distances are 2.815(2) Å, which is 1.047 times the mean distance in the prism. If d is the edge of an ideal rhombic prism the remaining distances in the model become 1.065 d . This means that the octahedra and the icosahedra in the observed structure are distorted in the same way and to almost the same degree as the octahedral and icosahedral interstices in the framework of ideal rhombic prisms.

Skutterudite itself and the other compounds containing arsenic or phosphorus are all a little more distorted due to the strong tendency these two elements have to form square-planar As_4 and P_4 groups (8). The rhombic prisms then become elongated in the direction shown in Fig. 5. This deformation of the prisms is easily achieved from the rotation of octahedra (6), and that is why the octahedral model is more useful in dealing with CoAs_3 , CoP_3 and $\text{LaFe}_4\text{P}_{12}$.

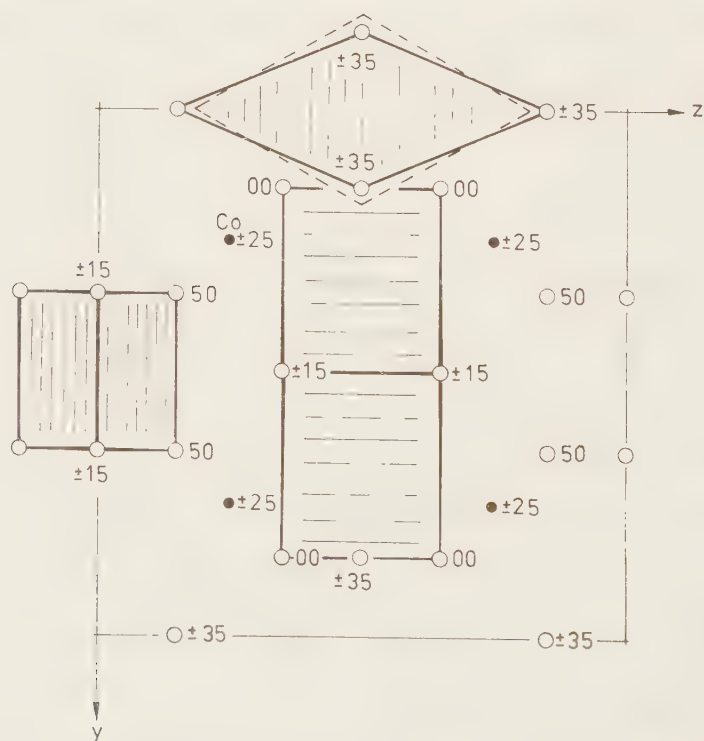


Fig. 5. The structure of skutterudite, CoAs_3 . Only three rhombic prisms are indicated. Ideal prism in hatched lines.

The octahedral and icosahedral interstices of the rhombic prism framework can also be filled up in different ways and these are given in Table II.

Table II. The polyhedra occupied in the skutterudite type structure.

	<u>icosahedra</u>	<u>octahedra</u>	<u>rhombic prisms</u>
CoAs_3	-	Co	-
CoP_3	-	Co	-
Sc(OH)_3	-	Sc	-
WAl_{12}	W	-	-
$\text{NaMn}_7\text{O}_{12}$	Na	Mn	Mn
$\text{CaCu}_3\text{Mn}_4\text{O}_{12}$	Ca	Mn	Cu
$\text{ThCu}_3\text{Mn}_4\text{O}_{12}$	Th	Mn	Cu
$\text{LaFe}_4\text{P}_{12}$	La	Fe	-
CuTa_2O_6	-	Ta	Cu

CuTa_2O_6 (16) is not strictly isostructural with the rest of the group, but it is closely related. It crystallizes in the orthorhombic space group Pmmm with $a = 7.5228(9) \text{ \AA}$, $b = 7.5248(9) \text{ \AA}$ and $c = 7.5199(9) \text{ \AA}$. The $24(g)$ position in space group $\text{Im}3$ is split into six different fourfold positions, as shown below.

	O_1	O_2	O_3	O_4	O_5	O_6
x	0	0.186	0.305	1/2	0.312	0.191
y	0.304	0	0.188	0.191	1/2	0.310
z	0.187	0.305	0	0.312	0.192	1/2

Since these figures are close to those given in Table I, CuTa_2O_6 can be considered as a member of the skutterudite family. O_1 makes up the central square of a rhombic prism surrounding one Cu atom, O_2 does the same to another Cu atom and so on. The prisms created by O_4 , O_5 and O_6 are partly ($\approx 0,35$) occupied by Cu atoms while the others are fully occupied. In spite of this, there is no significant difference between the two kinds of prisms, but comparison shows that the Oftedal relation seems to be followed more closely by the partly occupied prisms.

It is an interesting fact that the rhombic prism occurs even in structures which lack atoms that prefer the square-planar arrangement, e.g. there is no obvious reason why $\text{Sc}(\text{OH})_3$ and WAl_{12} should be of the skutterudite-type structure. These compounds, with their rhombic prisms empty, serve to show the importance of this particular arrangement of atoms, in the description of structures.

2. THE PYROCHLORE UNIT

The pyrochlore unit is a group of five octahedra sharing faces in a way that gives this unit T_d symmetry (Fig. 6). This unit can also be described as four interpenetrating columns of *hcp* with each column consisting of two face-sharing octahedra. The name "pyrochlore unit" originates from a group of oxides, halides and oxyhalides, called pyrochlores, which have this particular arrangement of octahedra (17, 18).

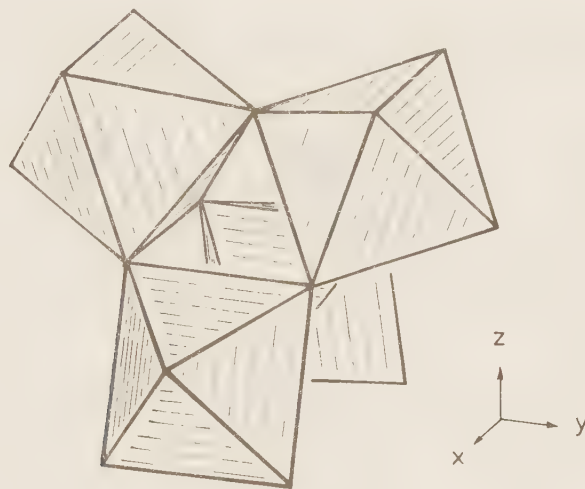


Fig. 6. The pyrochlore unit.

In pyrochlore itself the units share corners in a three-dimensional array shown in Fig. 7, but in some other structures separate units also occur.

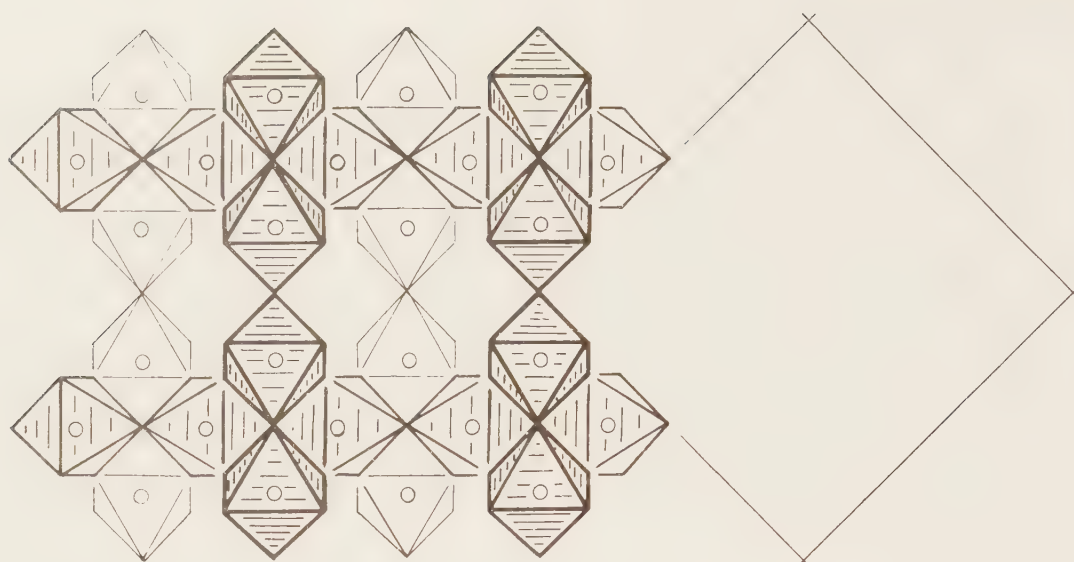


Fig. 7. The octahedral framework of the pyrochlore structure.

The octahedral framework of pyrochlore is made up of atoms in position 48(f), $x, 0, 0$, of space group $Fd3m$. To get regular octahedra the parameter x has to be,

$$x = \frac{1}{2(\sqrt{3} \frac{3}{2} \theta + 1)} = \frac{3}{16} = 0.1875 \quad (3)$$

where θ is the dihedral angle of a regular tetrahedron (19).

Table III lists the x -values of some compounds which have the pyrochlore structure.

Table III. The parameters of the 48(f) position of Fd3m which defines the octahedral framework in the pyrochlore structure.

E = empty octahedra and F = filled octahedra. ("Filled" means that the outer four octahedra of a pyrochlore unit are centered with atoms.)

	x	Ref.
Framework of regular octahedra	$\frac{3}{16} = 0.1875$	(3)
F $[(\text{Na,Ca})_2(\text{Nb,Ti})_2(\text{O,F})_6(\text{O,F})]$, pyrochlore	0.195	(18)
E Sb_2O_3	0.186	(20)
F RbNbTeO_6	0.180	(18)
F $\text{Al}_{2+x}(\text{OH})_6\text{F}_{3x}$	0.1875	(21)
F $[\text{K}_{1.14}\text{Bi}_{0.37}^{\text{III}}][\text{Bi}_{0.27}^{\text{III}}\text{Bi}_{1.73}^{\text{V}}][\text{O}_{4.9}\text{OH}_{1.1}]\text{OH}_{0.8}$	0.199	(22)
F $\text{W}_3\text{Fe}_3\text{C}$	0.198	(23)
E ₁ $\text{W}_6\text{Fe}_6\text{C}$	0.197	(23)
F $\text{W}_4\text{Co}_2\text{C}$	0.195	(24)
E NiTi_2	0.185	(25)
E $\text{Cr}_4\text{Al}_{13}\text{Si}_4$ *	0.185	(26)

* $\text{Cr}_4\text{Al}_{13}\text{Si}_4$ crystallizes in the space group $\text{F}\bar{4}3\text{m}$, which splits the 48(f) position of Fd3m into two 24-fold positions, 24(f) and 24(g). The x-value 0.185 is transformed from the parameters given for the two 24-fold positions of $\text{F}\bar{4}3\text{m}$.

The figures in Table III show that the octahedra are distorted.

An x-value larger than $\frac{3}{16}$ expands the central octahedron of the pyrochlore unit and this leads to a compression of the other octahedra along a three-fold axis; an x-value smaller than $\frac{3}{16}$ does the opposite.

The rigidity of the "pyrochlore framework" is illustrated in the compounds W_3Fe_3C and W_6Fe_6C with carbon occupying different positions in the two structures. In W_6Fe_6C the central octahedron of each pyrochlore unit is occupied, but in W_3Fe_3C it is empty and the other four are filled with carbon. Furthermore, Table III does not show any significant difference between filled and empty pyrochlore frameworks.

The pyrochlore framework can also be broken up into single pyrochlore units and one way to do this is to expand every alternate central octahedron, as defined earlier, into a truncated tetrahedron (3). This enlargement of the framework makes enough room for another similarly blown up pyrochlore framework to interpenetrate (Fig. 8). The space group remains $Fd3m$ and the pyrochlore units are now defined by position 48(f), $x, 0, 0$, and position 96(g), x, x, z . The parameters of a structure built up of ideal pyrochlore units separated by ideal truncated tetrahedra are calculated and compared with some known compounds with this structure in Table IV.

Table IV. The parameters of the 48(f) and 96(g) positions of space group $Fd3m$.

	48(f)	96(g)		Ref.
	x	x	z	
Calc.	0.136	0.068	0.303	(3)
$Mg_3Cr_2Al_{18}$	0.141	0.067	0.300	(27)
$VA1_{10}$	0.141	0.065	0.301	(28)
$ZnZr_{22}$	0.140	0.063	0.305	(29)

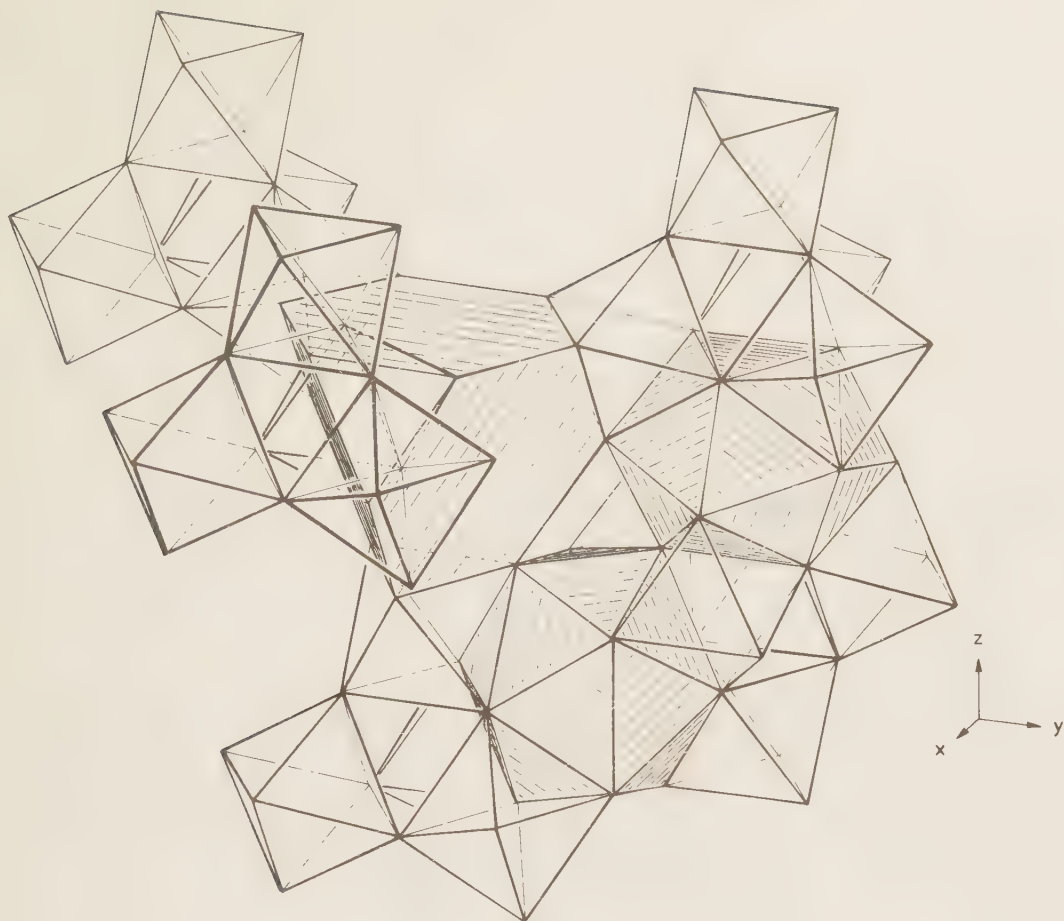


Fig. 8. Part of the $\text{Mg}_3\text{Cr}_2\text{Al}_{18}$ structure; four pyrochlore units sharing faces with a truncated tetrahedron. In the lower right part of the figure, one pyrochlore unit from the second pyrochlore-truncated tetrahedra framework is inserted to show the creation of two icosahedra.

The structure of U_2F_9 and NaTh_2F_9 (isostructural) (30) shows another way to arrange the pyrochlore units (Fig. 9, 10). The space group is $I\bar{4}3m$, and the fluorine atoms in the positions 24(g), x, x, z , and 12(e), $x, 0, 0$, define the pyrochlore units. These units are empty and connected to each other through U(Th)-centered trigonal prisms (Fig. 10). In NaTh_2F_9 , four sodium atoms are said to be in the 6-fold position 6(b), surrounded by a distorted enlarged octahedra of fluorine atoms.

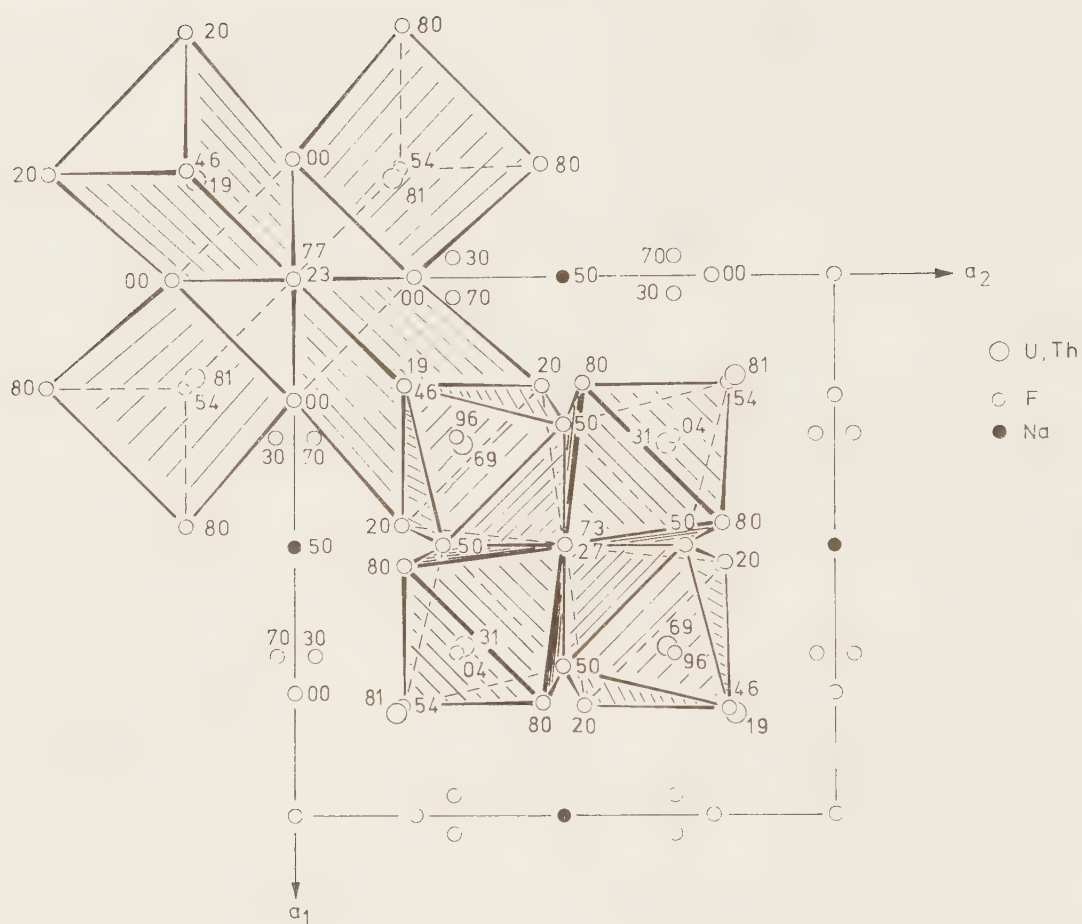


Fig. 9. The structure of U_2F_9 (or NaTh_2F_9) projected along 001. The slightly distorted pyrochlore unit which is seen in the centre of the figure has a common face with one of the corner-sharing trigonal prisms in the upper left part of the figure.

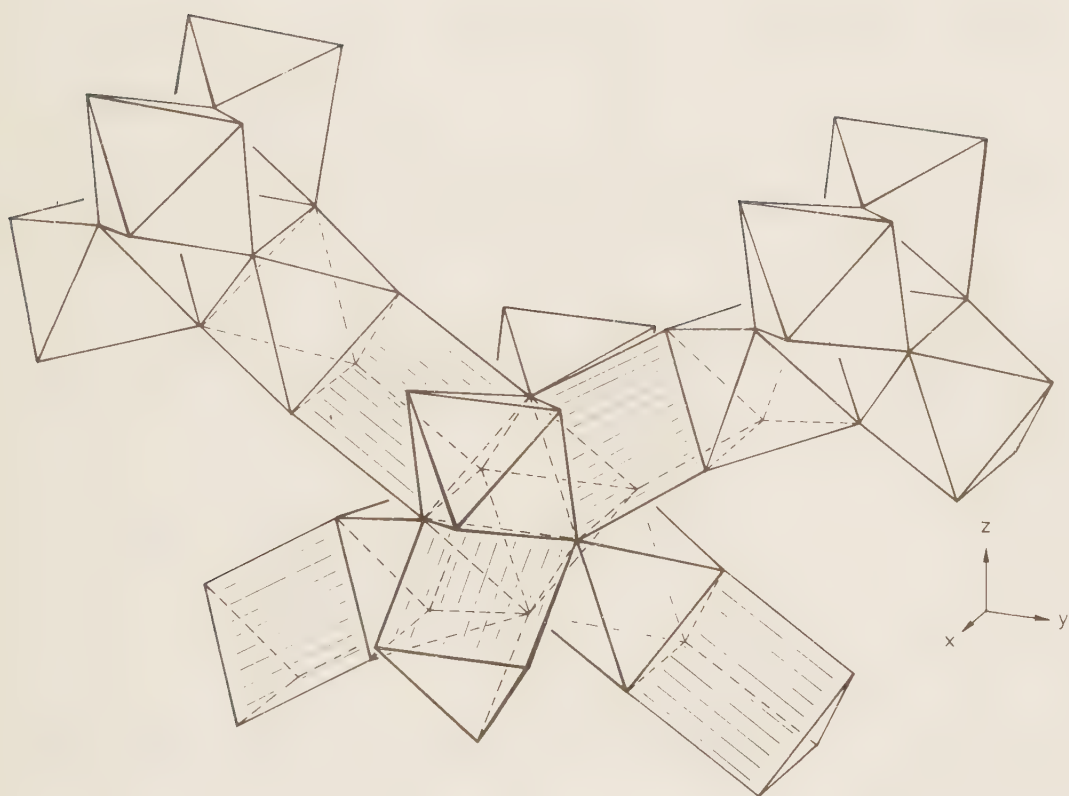


Fig. 10. Part of the U_2F_9 structure. The pyrochlore units are connected to each other through trigonal prisms.

The ideal parameters (ideal octahedra + ideal trigonal prisms with the edge = d) can be calculated as follows:

Unit cell edge

$$a = \frac{\frac{4d\sqrt{2}}{\sqrt{3}} + 2d}{\sqrt{3}} = \frac{2d(2\sqrt{2} + \sqrt{3})}{3} \approx 3.040 d$$

Positions defining the pyrochlore units

$$12(e) \quad x = \frac{\frac{d\sqrt{2}}{2}}{\frac{2d(2\sqrt{2} + \sqrt{3})}{3}} = \frac{3}{8 + 2\sqrt{6}} \approx 0.2326$$

$$24(g) \quad x = \frac{\frac{d}{\sqrt{3}}}{\frac{2d(2\sqrt{2} + \sqrt{3})}{3}} = \frac{\sqrt{3}}{2(2\sqrt{2} + \sqrt{3})} \approx 0.1899$$

$$24(g) \quad z = \frac{3(\frac{d}{\sqrt{3}} + \frac{d\sqrt{2}}{\sqrt{3}})}{2d(2\sqrt{2} + \sqrt{3})} = \frac{\sqrt{3}(1 + \sqrt{2})}{2(2\sqrt{2} + \sqrt{3})} \approx 0.4584$$

Table V gives the calculated and observed parameters of the U_2F_9 structure type.

Table V. The parameters of the U_2F_9 structure type.

	12(e)	24(g)	Ref.
	x	x	z
Calc.	0.2326	0.1899	0.4584
U_2F_9	0.225	0.20	0.46 (30)
$NaTh_2F_9$	0.235	0.19	0.465 (30)

The agreement between the model and the real structures is very good. The small distortion of the ideal structure is different from the type of distortion in ordinary pyrochlore mentioned earlier. The four outer octahedra in the pyrochlore unit are not only compressed along a three-fold axis but the triangular faces common to the trigonal prisms, are also enlarged (Fig. 9, 10).

The other way to describe the structure is to use corner-connected tri-capped trigonal prisms but this makes the triangular faces mentioned above *smaller* than ideal, and this makes it impossible to build a model of the structure with ideal tri-capped prisms.

In the next chapter we will return to the pyrochlore structure and take into account also the remaining atoms in the structure.

3. THE "STELLA QUADRANGULA"

An interesting structure-building unit is the stella quadrangula (shortened to SQ in the following text). A SQ is a central tetrahedron sharing faces with four tetrahedra (Fig. 11). The symmetry of the SQ is T_d , the same as the symmetry of the pyrochlore unit.

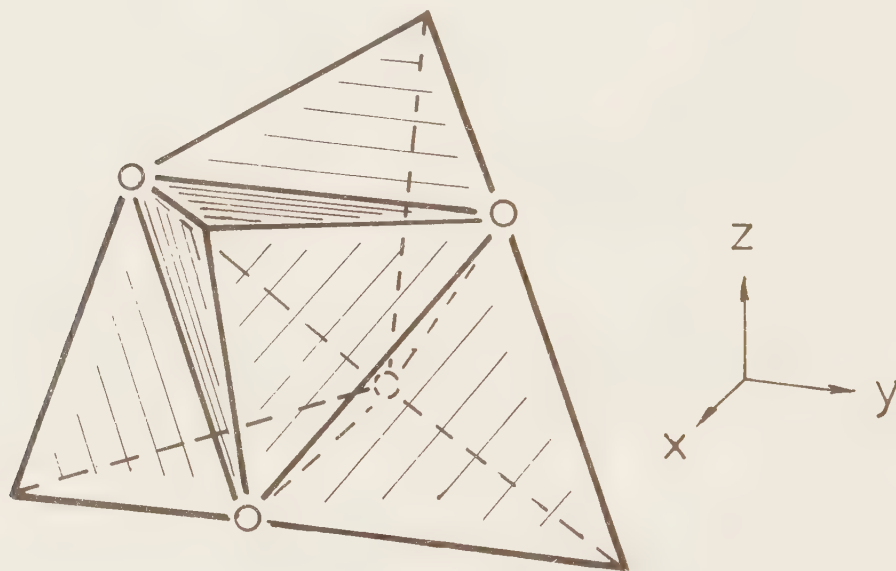


Fig. 11. The "stella quadrangula".

By connecting these SQs to each other in different ways, many known structure types can be obtained (3, 4, 5). Some of the tetrahedra of the SQ can be filled with atoms, as in the ionic compounds SiF_4 , scheelite and $\text{Ba}_3\text{Fe}_3\text{Se}_7$ (31) or left empty as in most alloys containing SQs (3, 4).

The importance of the SQ as a building unit is considerably extended by capping the edges of both the inner and the outer tetrahedra and the ideally capping makes an edge of the polyhedron also the edge of an equilateral triangle. If only the edges of the inner tetra-

hedron are capped the result is the Mn-framework building unit, of the $\text{Th}_6\text{Mn}_{23}$ structure type (4). If, in addition, the edges of the outer tetrahedra are also capped the result is a γ -brass cluster (Fig. 12) (4).

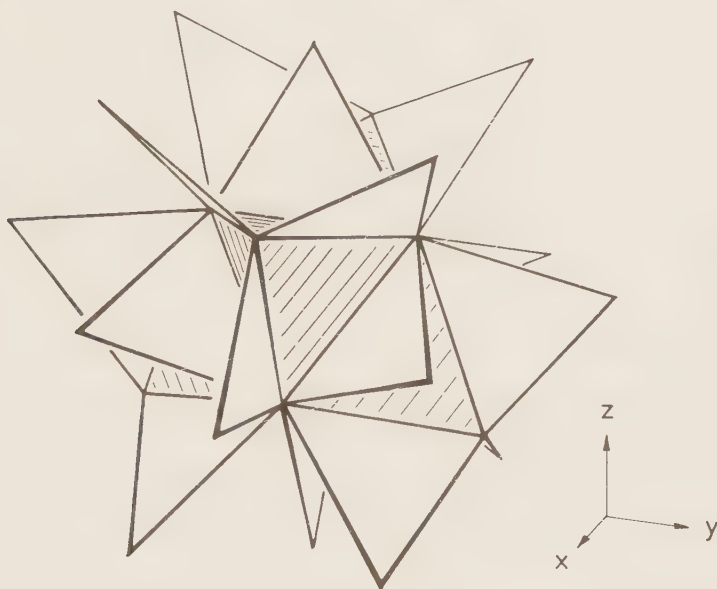


Fig. 12. The 26-atom γ -brass cluster.

The remaining part of the pyrochlore structure, i.e. the atoms that occupy positions in the tunnels of the octahedral framework, does in fact make up a second framework that interpenetrates the octahedral one. This second framework can be described as corner-connected SQs as shown in Fig. 13.

Positions 32(e), of space group $\text{Fd}3\text{m}$ define the inner tetrahedron and position 16(d) the outer tetrahedra of the SQs (3). In Table VI some observed parameters of the 32(e) and the 16(d) positions are compared with the values calculated from the ideal SQ framework.

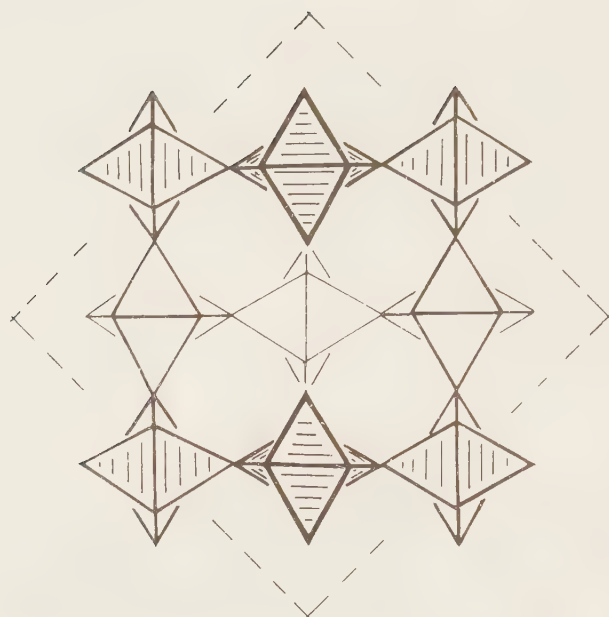


Fig. 13. Corner-sharing SQs. One of the two interpenetrating frameworks of the pyrochlore structure.

Table VI. The parameters of positions 32(e) and 16(d) of space group Fd3m which define the SQ network of the pyrochlore structure.

	32(e)	16(d)	Ref.
	x		
Ideal SQs	0.825	$\frac{5}{8}$	(3)
$K_{1.14}Bi_{2.37}O_{4.9}OH_{1.9}$	0.840	$\frac{5}{8}$	(22)
W_3Fe_3C	0.8297	$\frac{5}{8}$	(23)
W_6Fe_6C	0.8292	$\frac{5}{8}$	(23)
W_4Co_2C	0.825	$\frac{5}{8}$	(24)
$NiTi_2$	0.840	$\frac{5}{8}$	(25)

Table VI shows good agreement between the model and the observed structures. However, these two good models for the pyrochlore structure do not fit together. There is a metric size ratio of $\frac{d_{\text{oct}}}{d_{\text{tetr}}} = 1.25$ between the two ideal interpenetrating structures (3).

(A similar misfit between octahedra and tetrahedra exists in some layer silicates e.g. asbestos.)

In the $\text{Cr}_4\text{Al}_{13}\text{Si}_4$ structure (26) the inner tetrahedra of the SQs are made up of chromium atoms and the outer tetrahedra out of silicon atoms. The aluminium atoms make up the octahedral framework, but in addition, every alternate inner Cr_4 -tetrahedra is replaced by a single aluminium atom. This makes another description of the structure possible. Instead of describing the Al-position as an octahedral pyrochlore array, it is now possible to cap the SQs with aluminium atoms in the way described earlier, and this gives the 26-atom γ -brass cluster (Fig. 14). The clusters are then connected by caps in the cubic zincblende fashion as shown in Fig. 15. All atoms, with the exception of the aluminium atoms that replace the Cr_4 -tetrahedra, are defined by this model.

The parameters of the γ -brass cluster model of the $\text{Cr}_4\text{Al}_{13}\text{Si}_4$ structure can be calculated. If d is the edge of a tetrahedron, then the unit cell edge is,

$$a = \frac{4}{\sqrt{2}} \left(\frac{d\sqrt{3}}{2} + \frac{d}{\sqrt{2}} \right) \sin\theta \approx 4.1951 d$$

where θ is the dihedral angle of a tetrahedron (19).

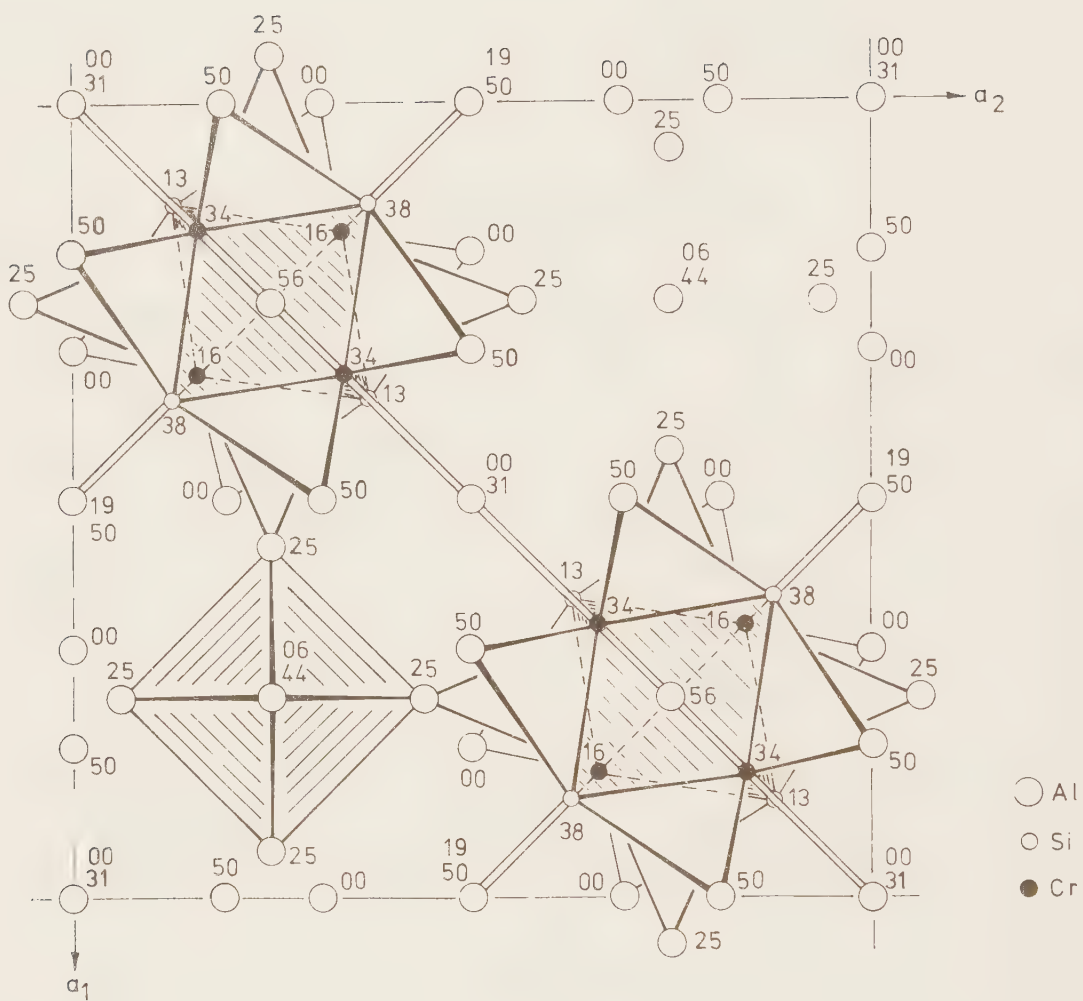


Fig. 14. Part of the $\text{Cr}_4\text{Al}_{13}\text{Si}_4$ structure. Two γ -brass clusters connected to each other over a cap are seen. In the lower left a central octahedron of a pyrochlore unit is indicated.

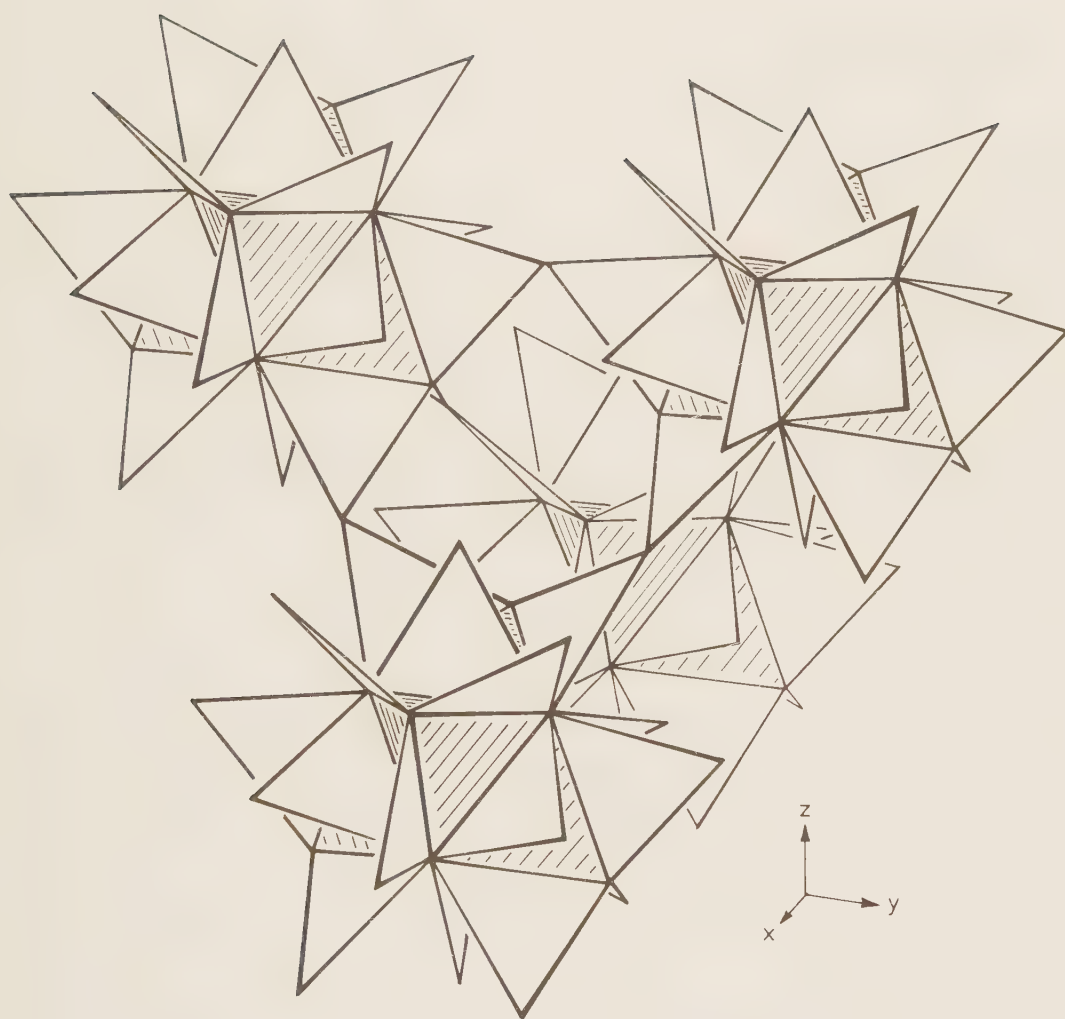


Fig. 15. The arrangement of γ -brass clusters in the $\text{Cr}_4\text{Al}_{13}\text{Si}_4$ structure.

The atomic parameters become:

$$\text{inner tetrahedron,} \quad x = \frac{\frac{d}{2\sqrt{2}}}{a} \approx 0.0843$$

$$\text{outer tetrahedron,} \quad x = \frac{\frac{5d}{6\sqrt{2}}}{a} \approx 0.1405$$

$$\begin{array}{l} \text{caps of the inner} \\ \text{tetrahedron,} \end{array} \quad x = \frac{\frac{d\sqrt{3}}{2} + \frac{d}{2\sqrt{2}}}{a} \approx 0.2907$$

$$\begin{array}{l} \text{caps of the outer} \\ \text{tetrahedra,} \end{array} \quad x = \frac{\frac{d}{2\sqrt{2}} - \left(\frac{d\sqrt{3}}{2} + \frac{d}{\sqrt{2}}\right) \cos \theta}{a} \approx -0.0407$$

In Table VII the two models of the structure are compared with the observed structure of $\text{Cr}_4\text{Al}_{13}\text{Si}_4$ (26). The origin is fixed by placing the centre of a SQ at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$.

Table VII. The parameters of the $\text{Cr}_4\text{Al}_{13}\text{Si}_4$ structure.

Space group $\text{F}\bar{4}3\text{m}$.

	4 Al(a)	16 Cr(e)	16 Si(e)	24 Al(f)	24 Al(g)
		x	x	x	x
Capped SQs	-	0.3343	0.1095	0.2907	0.5407
Pyrochlore units	-	-	-	0.3125	0.5625
$\text{Cr}_4\text{Al}_{13}\text{Si}_4$	0	0.3421	0.1260	0.3103	0.5600

Table VII shows that the pyrochlore units in the structure of $\text{Cr}_4\text{Al}_{13}\text{Si}_4$ are almost perfect and it is remarkable that the complete octahedral framework of pyrochlore can be generated by stacking capped SQs, γ -brass clusters, in the way shown in Fig. 15. According to the figures in Table VII, the clusters in $\text{Cr}_4\text{Al}_{13}\text{Si}_4$ are distorted and furthermore, the octahedra generated by the clusters are also distorted. As in the earlier case, there is a metric difference between the two models, this time with a ratio of $\frac{d_{\text{oct}}}{d_{\text{tetr}}} = 1.11$. But because the octahedra now are generated by the capped SQs, it is possible to build a model of the $\text{Cr}_4\text{Al}_{13}\text{Si}_4$ structure in spite of the different sizes of the octahedra and the tetrahedra.

The Mn-atom array of the common $\text{Th}_6\text{Mn}_{23}$ structure type (32) is very close to a model containing capped SQs (4).^{*} Only the inner tetrahedron of the SQ is capped and the SQs are connected by the caps (Fig. 16). The Th atoms, grouped as octahedra, are situated in the cavities of the SQ-framework. However the Th atoms can also be regarded as additional caps on the SQs, thereby completing the SQs to give the γ -brass clusters. Every Th atom is a cap of two SQs and therefore the caps have to be distorted (Fig. 17). There are two possibilities to distort the γ -brass cluster to such a degree that it can be connected as in $\text{Th}_6\text{Mn}_{23}$. Either the Th-atom caps are

^{*} In fact the model fits even better than reported in Ref. (4), due to a misprint. The correct figures of position 32(f) should be:

	x_{I}	x_{II}	Ref.
Calc.	0.0725	0.1208	(4)
$\text{Sr}_6\text{Mg}_{23}$	0.0726	0.1241	(33)

moved outwards from the SQ, or the Mn-atom caps are moved inwards. This means that position 24(e) of space group Fm3m should provide accomodation for bigger atoms or position 24(d) for smaller atoms. Table VIII shows that this is the case.

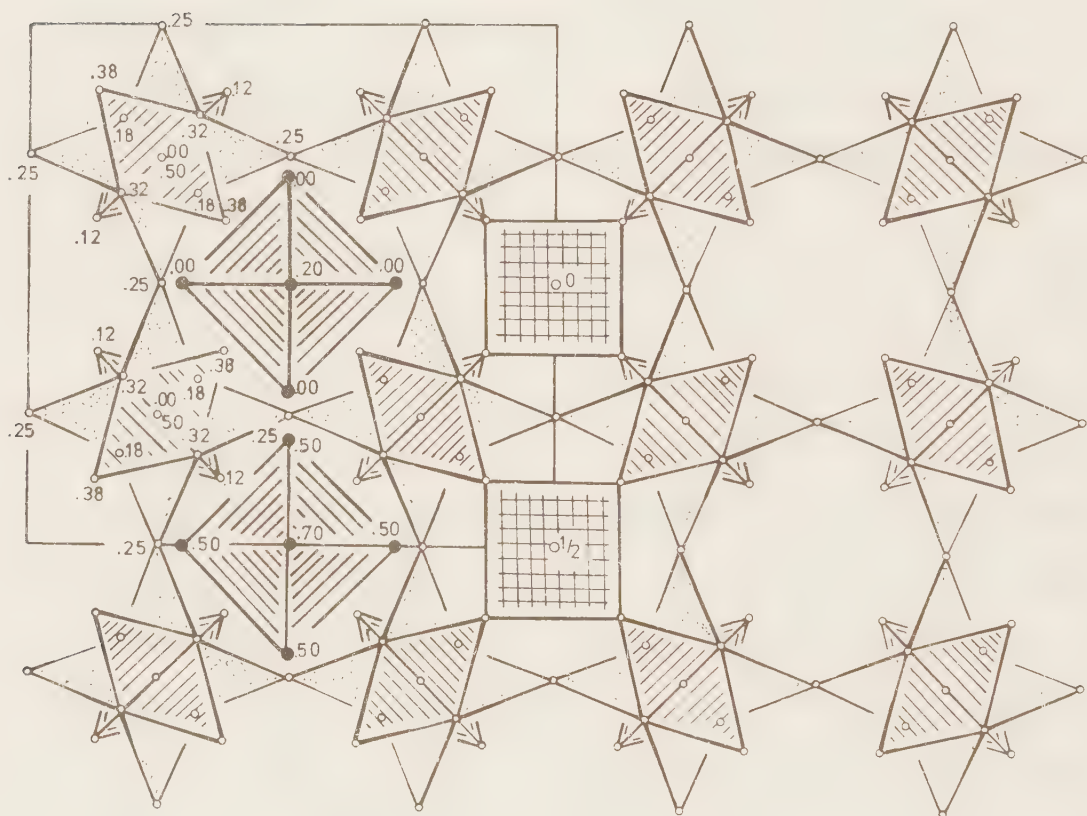


Fig. 16. The structure of $\text{Th}_6\text{Mn}_{23}$. Small rings are Mn atoms and filled rings are Th atoms.

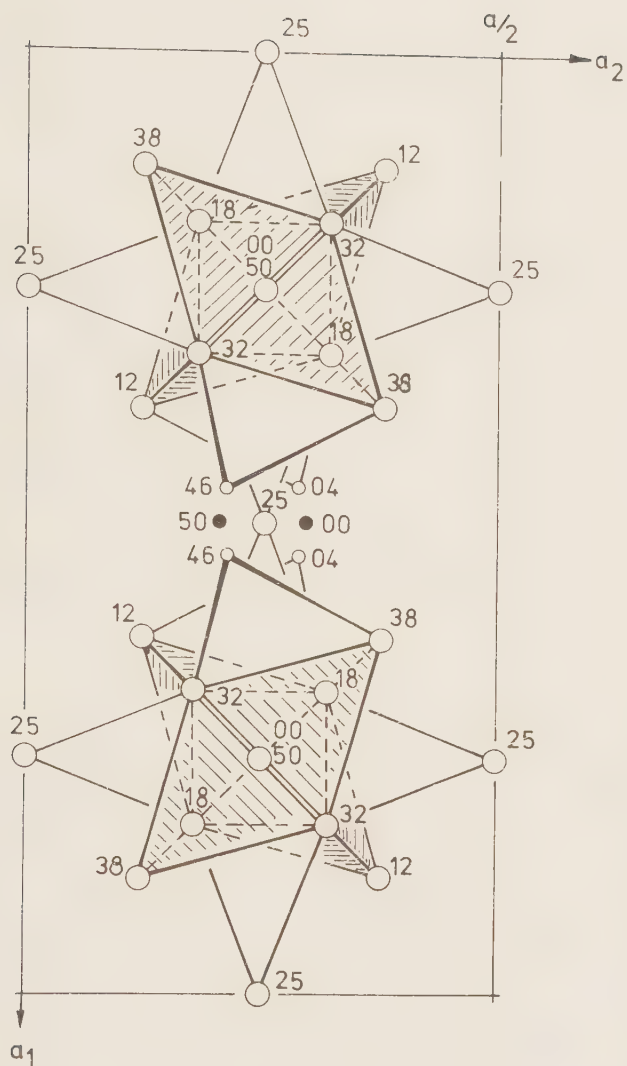


Fig. 17. Part of the $\text{Th}_6\text{Mn}_{23}$ structure. Large rings are Mn atoms. Small rings indicate the positions of four additional ideal caps on the SQs. Filled small rings show the actual Th atom position, a position which makes one Th atom able to cap both SQs but at the same time distort the ideal capping.

Table VIII. Atoms occupying positions 24(d) and 24(e) of the $\text{Th}_6\text{Mn}_{23}$ structure type. The radius ratio is also given.

	24(d)	24(e)	r_e/r_d^*	Ref.
$\text{Th}_6\text{Mn}_{23}$	Mn	Th	1.32	(32)
$\text{Sr}_6\text{Mg}_{23}$	Mg	Sr	1.32	(33)
$\text{Sr}_6\text{Li}_{23}$	Li	Sr	1.38	(33)
$\text{Ba}_6\text{Mg}_{23}$	Mg	Ba	1.35	(33)
$\text{Cd}_6\text{Mn}_{23}$	Mn	Gd	1.31	(34)
$\text{Mg}_6\text{Si}_7\text{Cu}_{16}$	Si	Mg	1.35	(35)
$\text{Ti}_6\text{Si}_7\text{Ni}_{16}$	Si	Ti	1.29	(36)

* Atomic radii are from *Interatomic Distances Supplement* (37).

All atoms of the $\text{Th}_6\text{Mn}_{23}$ structure, except the Mn atom in position 4(b), $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, are defined by this model of fully capped SQs.

In the γ -brass (Cu_5Zn_8) structure (38), the atoms are almost equal in size, (radius ratio = 1.04) and this makes the clusters close to ideal (4), and therefore impossible to stack in the $\text{Th}_6\text{Mn}_{23}$ manner. Instead the clusters are arranged in body-centered cubic array with no atoms common to more than one cluster. The space group is $I\bar{4}3m$ and the empty space between two clusters along the body diagonal is in fact a distorted $\text{Th}_6\text{Mn}_{23}$ -cluster which shares edges and corners with the γ -brass cluster. In Cu_5Zn_8 the inner tetrahedron and the caps on the outer tetrahedra are Zn atoms and the rest are Cu atoms. By changing the kind of atom in a certain position in every alternate cluster without any geometrical change of the

cluster, the space group changes to $P\bar{4}3m$, as in $NiCd_5$ (39) and Cu_9Al_4 (37). With four different, but geometrically equal clusters, the space group becomes $F\bar{4}3m$ and the unit cell edge is doubled, as in Pt_3Zn_{10} (40) and $Cu_{31}Sn_8$ (41). In some of these γ -brass type structures there are vacancies in the clusters, e.g., in $NiCd_5$ the inner tetrahedron of one type of cluster is vacant. Another way to describe this type of γ -brass is to extend the filled clusters by connecting them to the distorted Th_6Mn_{23} cluster in the way mentioned above. These extended clusters are connected to each other by sharing the remaining Th_6Mn_{23} caps and thereby the complete $NiCd_5$ structure is defined.

CONCLUDING REMARKS

As mentioned earlier, the choice of a model in the description of a crystal structure depends on the purpose for which it is described. Nevertheless, a good model must fit fairly well to the observed structures.

Our main purpose has been to find connections between ionic structures and alloy structures and we have found that one link between these two groups of structures is the *empty polyhedron*. An ionic structure, with one type of polyhedron filled, has an alloy-like cousin with that type of polyhedron empty and *vice versa*.

We have also found that there exist some very rigid arrangements of atoms, which seems to be little affected by the surrounding atoms. The rhombic prism framework in the skutterudite-type structure is almost unaltered whether the prisms are filled, partly filled or empty. The same rigidity is shown by the pyrochlore structure, and the most striking example is the NaZn_{13} structure. This structure, shown in Fig. 18, is built up of corner-connected SQs of Zn atoms in a way which creates interstitial snub cubes centered by Na atoms and icosahedra centered by Zn atoms (5). Na atoms can be substituted by K atoms with only a very small change in unit cell although the radius ratio = 1.22 (5).

The "stella quadrangula" is of great importance in the description of alloy structures. Single SQs or different arrangements of them, with or without capping, are found in several of the alloys with so called "giant cells", e.g. $\text{Rh}_7\text{Mg}_{44}$ (42), where also pyrochlore units appear.

The rhombic prism, the pyrochlore unit and the "stella quadrangula" have one (coincidental) property in common. They can all generate icosahedra. An icosahedron is generated when rhombic prisms are stacked in the "skutterudite way" (Fig. 19). In the structure of VAL_{10} (3) an icosahedron is created between two pyrochlore units (Fig. 20). SQs generate an icosahedron in the NaZn_{13} structure (Fig. 18) and the connecting Mn atom in position 24(d) of the $\text{Th}_6\text{Mn}_{23}$ structure is also surrounded by an icosahedron of 4 Th atoms and 8 Mn atoms (Fig. 16). The generated icosahedra are not regular but deformed in the same way as the icosahedra in the observed structures.

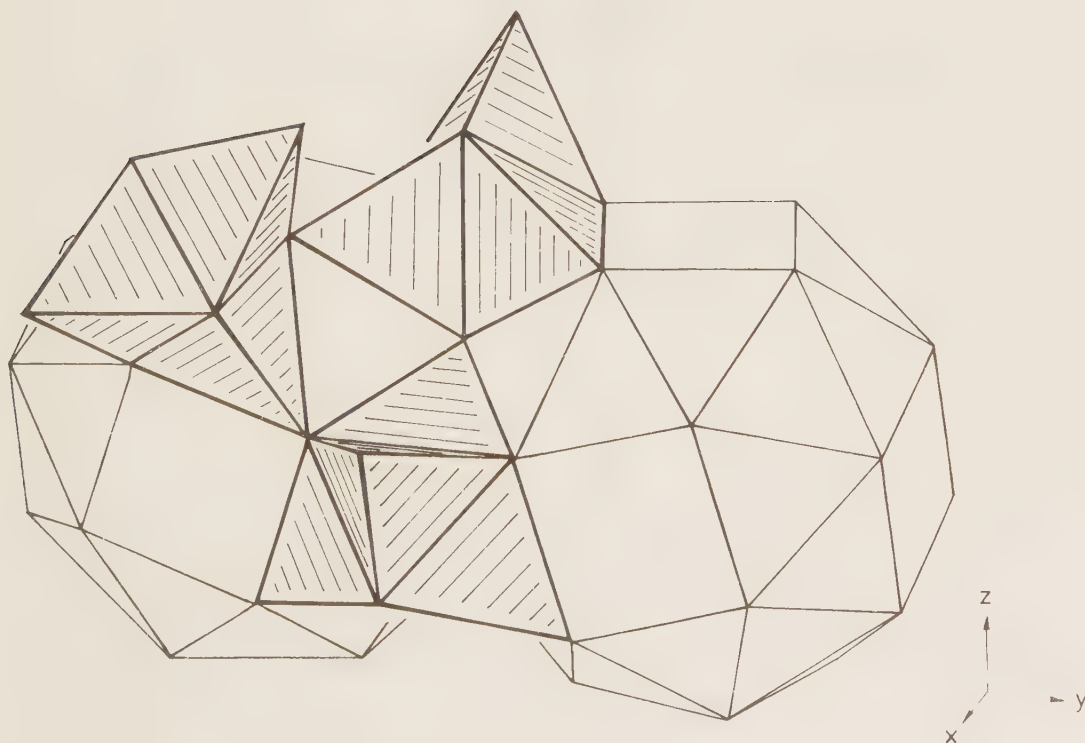


Fig. 18. Part of the NaZn_{13} structure.

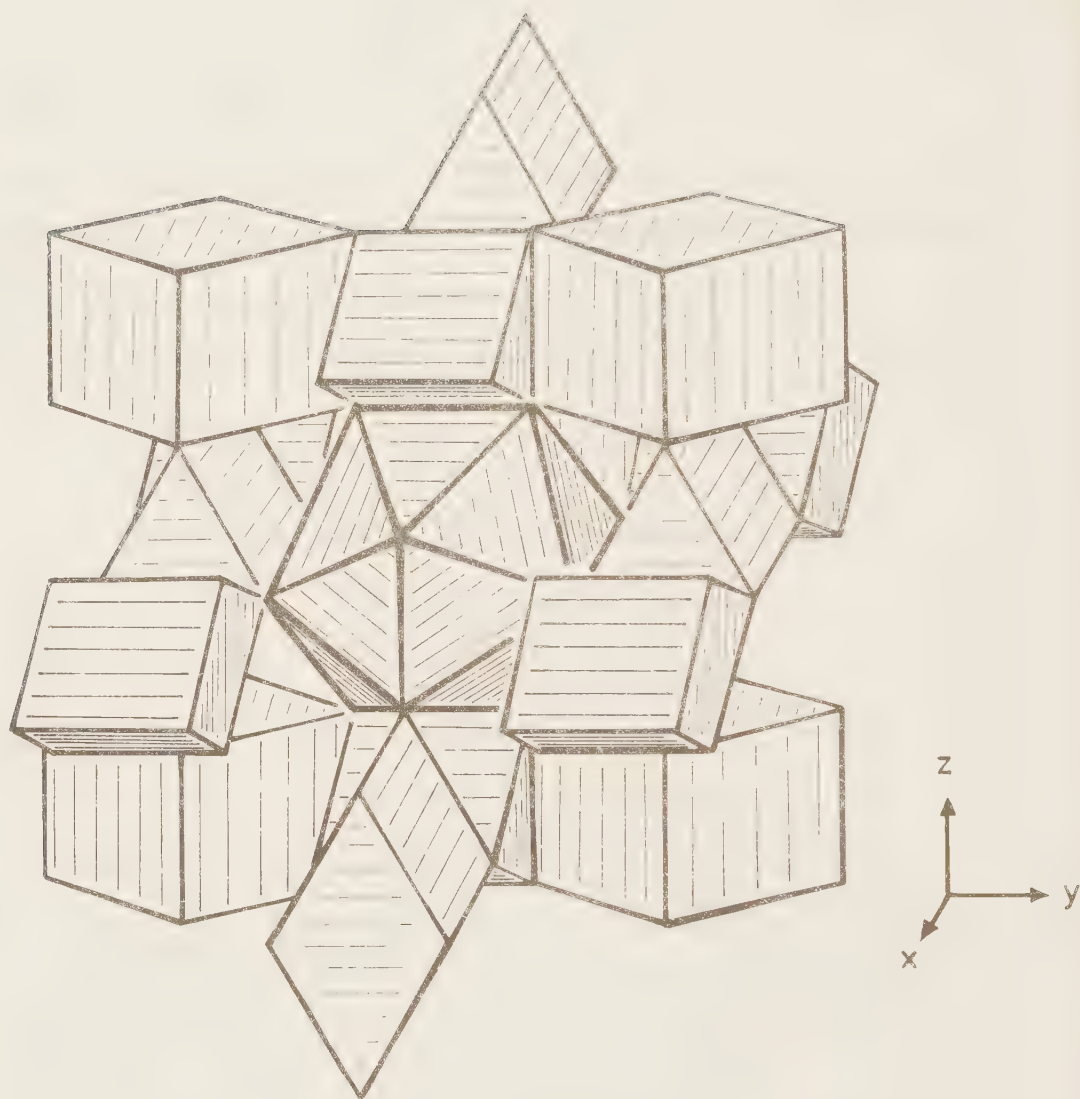


Fig. 19. An icosahedron is generated by rhombic prisms in the skutterudite-type structure.

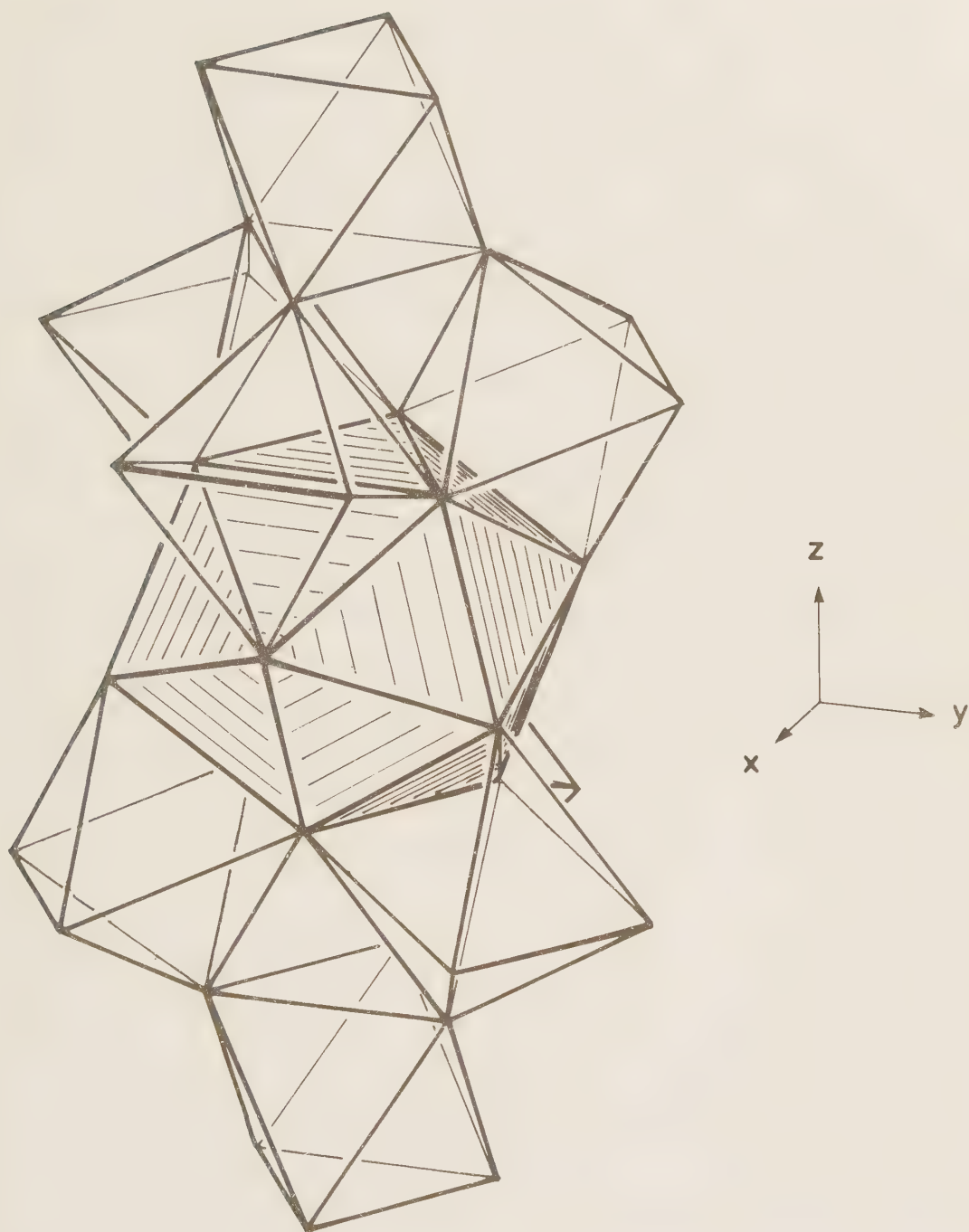


Fig. 20. An icosahedron is generated between two pyrochlore
units in the VAl_{10} structure.

ACKNOWLEDGEMENTS

I wish to thank Dr Sten Andersson and Prof. B.G. Hyde who have taught me almost everything I know about structures.

I am very grateful to the head of this department, Prof. Bengt Aurivillius, for facilities placed at my disposal.

Many thanks are also due to my colleagues at the department for stimulating discussions around the coffee-table.

A special word of thanks to Ms Eva-Lena Larsson, who typed this manuscript, for her unfailing support and help.

I also thank Mr L. Seiron for help with the photographic work.

Financial support from the Swedish Natural Science Research Council and the Royal Physiographic Society in Lund is gratefully acknowledged.

REFERENCES

1. Andersson S. and Hyde B.G. (1974) *J. Solid State Chem.* 9, 92
2. Nyman H. (1976) *J. Solid State Chem.* 17, 75
3. Nyman H., Andersson S., Hyde B.G. and O'Keeffe M. (1978)
J. Solid State Chem. 26, 123
4. Nyman H. and Andersson S. (1979) *Acta Crystallogr.* A35, 580
5. Nyman H. and Andersson S. (1979) To be published in *Acta Crystallogr.* A35
6. Hyde B.G. and O'Keeffe M. (1977) *Acta Crystallogr.* B33, 3802
7. Oftedal I. (1928) *Z. Kristallogr.* 66, 517
8. Rundqvist S. and Ersson N.-O. (1968) *Ark. Kemi* 30, 103
9. Schubert K. and Seitz A. (1948) *Z. Anorg. Chemie* 256, 226
10. Adam J. and Rich J.B. (1954) *Acta Crystallogr.* 7, 813
11. Marezio M., Dernier P.D., Chenavas J. and Joubert J.C. (1973)
J. Solid State Chem. 6, 16
12. Chenavas J., Joubert J.C. and Marezio M. (1975) *J. Solid State Chem.* 14, 25
13. Deschizeaux M.N., Joubert J.C., Vegas A., Collomb A.,
Chenavas J. and Marezio M. (1976) *J. Solid State Chem.* 19, 45
14. Jeitschko W. and Braun D. (1977) *Acta Crystallogr.* B33, 3401
15. Kjekshus A. and Pedersen G. (1961) *Acta Crystallogr.* 14, 1065
16. Vincent H., Bochu B., Aubert J.J., Joubert J.C. and Marezio M.
(1978) *J. Solid State Chem.* 24, 245
17. Jona F., Shirane G. and Pepinsky R. (1955) *Phys. Rev.* 98, 903
18. Darriet B., Rat M., Galy J. and Hagenmuller P. (1971) *Mat. Res. Bull.* 6, 1305

19. *International Tables for X-ray Crystallography* (1967) Vol. II.
Kynoch Press, Birmingham, p. 47
20. Svensson C. (1975) *Acta Crystallogr.* B31, 2016
21. Cowley J.M. and Scott T.R. (1948) *J. Am. Chem. Soc.* 70, 105
22. Trehoux J., Abraham F. and Thomas D. (1977) *J. Solid State Chem.* 21, 203
23. Bojarski Z. and Leciejewicz J. (1967) *Ach. Hutn. Polska* 12, 255
[*Struct. Repts.* 32A, 45 (1967)]
24. Kiessling R. (1952) *Proc. Internat. Symposium on the Reactivity of Solids. Gothenburg.* Elanders Boktryckeri AB, p. 1065
[*Struct. Repts.* 18, 80 (1954)]
25. Yurko G.A., Barton J.W. and Parr J.G. (1959) *Acta Crystallogr.*
12, 909
26. Robinson K. (1953) *Acta Crystallogr.* 6, 854
27. Samson S. (1958) *Acta Crystallogr.* 11, 851
28. Brown P.J. (1957) *Acta Crystallogr.* 10, 133
29. Samson S. (1961) *Acta Crystallogr.* 14, 1229
30. Zachariasen W.H. (1949) *Acta Crystallogr.* 2, 390
31. Hong H.Y. and Steinfink H. (1972) *J. Solid State Chem.* 5, 93
32. Florio J.V., Rundle R.E. and Snow A.I. (1952) *Acta Crystallogr.*
5, 449
33. Wang F.E., Kanda F.A., Miskell C.F. and King A.J. (1965) *Acta Crystallogr.* 18, 24
34. Wang F.E., Gilfrich J.V., Ernst D.W. and Hubbard W.M. (1964)
Acta Crystallogr. 17, 931
35. Bergman G. and Waugh J.L.T. (1956) *Acta Crystallogr.* 9, 214
36. Beattie H.J. Jr and Ver Snyder F.L. (1956) *Nature* 178, 208

37. *Interatomic Distances Supplement*, special publication No. 18,
The Chemical Society, London
38. Bradley A.J. and Jones P. (1933) *J. Inst. Metals* 51, 131
39. Ljung H. and Westman S. (1970) *Acta Chem. Scand.* 24, 611
40. Johansson A. and Westman S. (1970) *Acta Chem. Scand.* 24, 3471
41. Knödler H. (1964) *Metall* 18, 1172
42. Andersson S. (1978) *Acta Crystallogr.* A34, 833
43. Pythagoras (~540 B.C.)

APPENDIX

The mathematics used in this work can be expressed in the following equation:

$$c^2 = a^2 + b^2 \quad (43)$$

where a , b and c are the length of the sides of a right-angled triangle (Fig. 21).

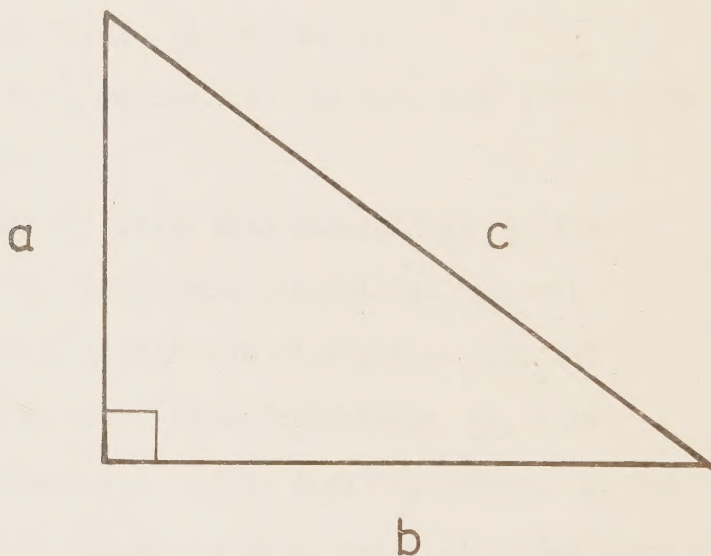


Fig. 21. A right-angled triangle.

